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A review of the biological effects of acid-iron wastes from titanium dioxide production in the United Kingdom

by

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INTRODUCTION

It has long been recognized that the titanium dioxide (TiO_2) extraction process is exceptional in terms of its effluent type and quantity, and that considerable care must be taken in the siting of a factory to ensure that natural resources are used to maximum advantage in safeguarding the environment. It is largely for this reason that the two major United Kingdom TiO_2 factories were located on the Humber Estuary, which receives water from a catchment area of approximately 27 000 km^2 (almost 20% of England) and has a very large flow (21 million m^3/day average freshwater flow), thus ensuring fairly rapid dilution and dispersion before discharging to the sea.

The two factories started production 20-25 years ago. Since then they have expanded and other industries have been established in the same area, including the manufacture of fertilizers, fibres, plastics and pharmaceuticals and oil refining. One of the TiO_2 companies, British Titan Products Company Limited, considered it appropriate as far back as 1957 to institute chemical and biological investigations of the area into which their effluent was discharged. This paper summarizes very briefly some of the main results both of these investigations and of studies carried out by the Fisheries Laboratory, Burnham-on-Crouch. The intention is to illustrate the extent of data available in the UK; at this stage the significance of the results is not discussed in detail. Reference is not made to other research work on this subject, since most of it is well documented and available from the literature.

We are indebted to British Titan Products Company Limited for allowing us to use the results of their investigations and associated research carried out by Queen Mary College, London, and for their willingness to make more detailed information available to ICES at a later date.

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PHYSICAL AND CHEMICAL CHARACTERISTICS OF THE ACID-IRON WASTE FROM THE SULPHATE PROCESS

Acid-iron wastes are the by-product of the acid extraction of ores during the production of titanium dioxide, and their precise composition depends on the extraction process and on the origin of the ore. For example, a typical waste from a sulphate process operating on ilmenite contains 2% free sulphuric acid, 0.1-0.2% suspended solids, and 0.8% soluble iron, with very much smaller quantities of titanium, chromium, vanadium and zinc. The solids are made up largely of unattacked ore, titanium dioxide and silica. The most obvious characteristic of the waste is its acidity and at high concentrations it produces a marked reduction in the pH of sea water (Figure 1). With increasing dilution by sea water the pH rises rapidly and the soluble ferrous iron precipitates and oxidizes to hydrated ferric oxide, producing the characteristic orange-brown floc. This reaction produces a considerable chemical oxygen demand in the water.

The British Titan effluent discharges continuously just below the level of mean low water into shoal water of the Humber Estuary at a rate of 22 700 m^3/day. Since the estuary is tidal the direction of flow past the outfall changes from ebb to flood, with a period of slack water at high and low tide. Current speeds can reach 4 km/hour. The tidal excursion is always considerable and is related to tidal range such that a neap tide of 2 m has an excursion of some 8 km but a spring tide of 6 m has an excursion in excess of 17 km. The size and shape of the effluent plume will therefore be primarily dependent on the state of the tide (Figure 2), with the effluent forming a virtually undiluted pool off the outfall at slack water. During flood and ebb there is dilution along the narrow plume with increasing distance from the outfall (Figure 3). Surveys of dissolved oxygen, salinity, pH, suspended solids, iron and sulphate of the estuary water from 1964 to the present time have not demonstrated any changes that can be attributed to this effluent. Changes have occurred in the sediments of the immediate area. Close to the outfall pipe there is a hard ferric crust overlying the substrate, and the presence of iron in the surface mud layers for several hundred metres on either side is clearly seen by the discoloration. Chemical analysis of samples shows the presence of titaniferrous material close to the outfall but beyond this zone the figures tend to be comparable with background levels.

BIOLOGICAL EFFECTS OF ACID-IRON WASTES

(a) Field observations

Two approaches have been adopted in order to study the ecological impact of the effluent discharge. Long-term effects have been assessed by regular surveys of benthic and planktonic organisms, and short-term effects have been studied by using caged animals anchored within the area influenced by the effluent plume.

Surveys of the intertidal zone have been carried out for over 15 years at selected stations on both the south and north shore of the estuary so that any changes in fauna adjacent to the outfall can be assessed in the context of natural fluctuations in the estuary as a whole. It is not possible to reproduce the extensive results of these regular surveys here, but Table 1 shows the range of typical estuarine species encountered at two stations in 1957 and 1971. Although a decline in species diversity on the south shore has occurred over this period, the range of benthic species has always been less on the non-industrialized north shore. The histograms in Figure 4 illustrate that whilst there has been a decline in the level of abundance of some species (e.g. Macoma balthica) at certain sites from 1959 to 1972, others have maintained their level or even increased it somewhat (e.g. Nereis diversicolor), so that the biomass of much of the south shore has remained high.

Overall, therefore, it can be stated that although there are natural differences in the fauna and flora at the selected stations in the estuary there have been changes on the south bank over the period of investigation. It is not clear, however, to what extent these are due to the summated effects of industrial and other discharges or to natural hydrographic and climatic changes. Certainly, the British Titan effluent has an impact on the benthos in the area adjacent to the outfall. There is a small elliptical area near the pipe which is virtually abiotic. Outside this area nematodes and Nephtys sp. occur with increasing abundance and size with distance from the pipe. Beyond this zone Macoma, Cardium and epi-benthic species such as Carcinus and Crangon occur. The abiotic area is similar in shape to, but smaller than, the zone that was determined as lethal to caged shrimps and fish (Figure 5). This is presumably because the worms remain buried in the substrate and therefore out of direct contact with the pool of acidified water that is evident at slack water (Figure 2).

(b) Laboratory observations

These were instigated to attempt to explain the observed distribution of animals in the field by obtaining a clearer understanding of the toxic mechanisms of the waste. Preliminary acute toxicity experiments showed that the 96 hour LC_{50}s for a wide variety of species (e.g. Pleuronectes, Pomatoschistus, Macoma, Nephtys) were in excess of 1000 parts/10^6, and more detailed experiments confirmed that, for most species, the median lethal threshold concentration lay between 2000 and 8000 parts/10^6 (Figure 6). In Figure 7 the toxicity curve for the waste has been compared with those for technical grade sulphuric and hydrochloric acids. Although major differences are obvious, when these curves are compared on the basis of concentration a unified picture emerges if the survival times are plotted against the pH of the solutions. It therefore appears that the hydrogen ion concentration of the acid-iron waste is the active component for, at least, the short-term toxicity.

The possible presence and magnitude of long-term toxicity and sub-lethal effects have been investigated in a number of ways. For example, it has been found that only concentrations of waste in excess of 1000 parts/10^6 significantly depressed the growth rates of Artemia nauplii and juvenile Ophryotrocha (Figure 8) and caused a marked depression in the heart-rate (i.e. beats/unit time) of the fish Agonus cataphractus in less than 1 hour (Figure 9). Studies have been carried out on the effects of a concentration of the waste of 250 parts/10^6 on the growth of Ophryotrocha over three generations, and it is clear from the results that no accumulative sub-lethal factors were evident in this time.

Whilst the absence of a species near the outfall might be the result of acute or chronic toxicity, it is possible, especially for fish and for mobile epibenthic species such as Crangon and Carcinus, that their absence is the result of a directed behavioural response. Indeed, Carcinus shows a marked ability to detect and avoid potentially lethal waters of low pH (Figure 10).

CONCLUSIONS

This paper summarizes very briefly some of the results of investigations carried out by the British Titan Products Company Limited and the Fisheries Laboratory, Burnham-on-Crouch on a piped discharge of acid-iron waste into the Humber Estuary.

From both field and laboratory studies it appears that the toxic effects of the acid-iron waste can be explained by its low pH. However, the waste is rapidly neutralized when diluted with sea water, so that at concentrations below 1000 parts/10^6 the pH approaches that of sea water and no acute or sub-lethal effects are evident.

In the case of the discharge to the Humber the build-up of effluent off the outfall at slack water has led to localized damage to the biota, but the large volume of the estuary, its alkalinity, high current speeds and turbulence ensure that great dilution and neutralization of the waste takes place subsequently. Precipitated iron evidently discolours many of the animals near the outfall, but initial analyses of mussels for Fe, Ti, Cu, Cr, Pb, V, Zn and As have not indicated any elevated levels in their tissues.

Although these studies have been concerned with effects of a piped discharge, the results are also very useful in assessing the possible biological consequences of sea dumping of acid-iron waste, because under the more restricted potential for dilution from outfalls toxic effects are more likely to be evident. The careful selection of dumping grounds where tidal velocities are high should prevent the occurrence of such effects in the open sea.

Table 1 Invertebrate species recorded at two stations in the intertidal zone of the Humber in 1957 and 1971

Group		South shore		North shore	
		1957	1971	1957	1971
ANTHOZOA	*Sagartia* sp.	+		+	+
POLYCHAETA	*Nereis diversicolor*	+	+	+	+
	Nereis virens		+		
	Lanice conchilega	+	+		
	Pectinaria koreni	+			
	Scoloples armiger	+	+		
	Arenicola marina	+	+	+	+
	Polydora ciliata	+			
	Nephtys sp.	+	+		
CRUSTACEA					
CIRREPEDIA	*Balanus balanoides*	+	+	+	+
ISOPODA	*Naesa* sp.				+
AMPHIPODA	*Gammarus zaddachi*	+	+	+	+
DECAPODA	*Crangon crangon*	+	+		
	Carcinus maenas	+	+	+	+
MOLLUSCA	*Littorina saxatilis*			+	+
	Littorina littorea	+	+	+	+
	Nucella lapillus	+			
	Buccinum undatum	+			
	Mytilus edulis	+	+		
	Cardium edule	+	+	+	+
	Macoma balthica	+	+	+	+
	Hydrobia sp.	+	+		+
	Mya sp.	+	+	+	
	Scrobicularia plana			+	

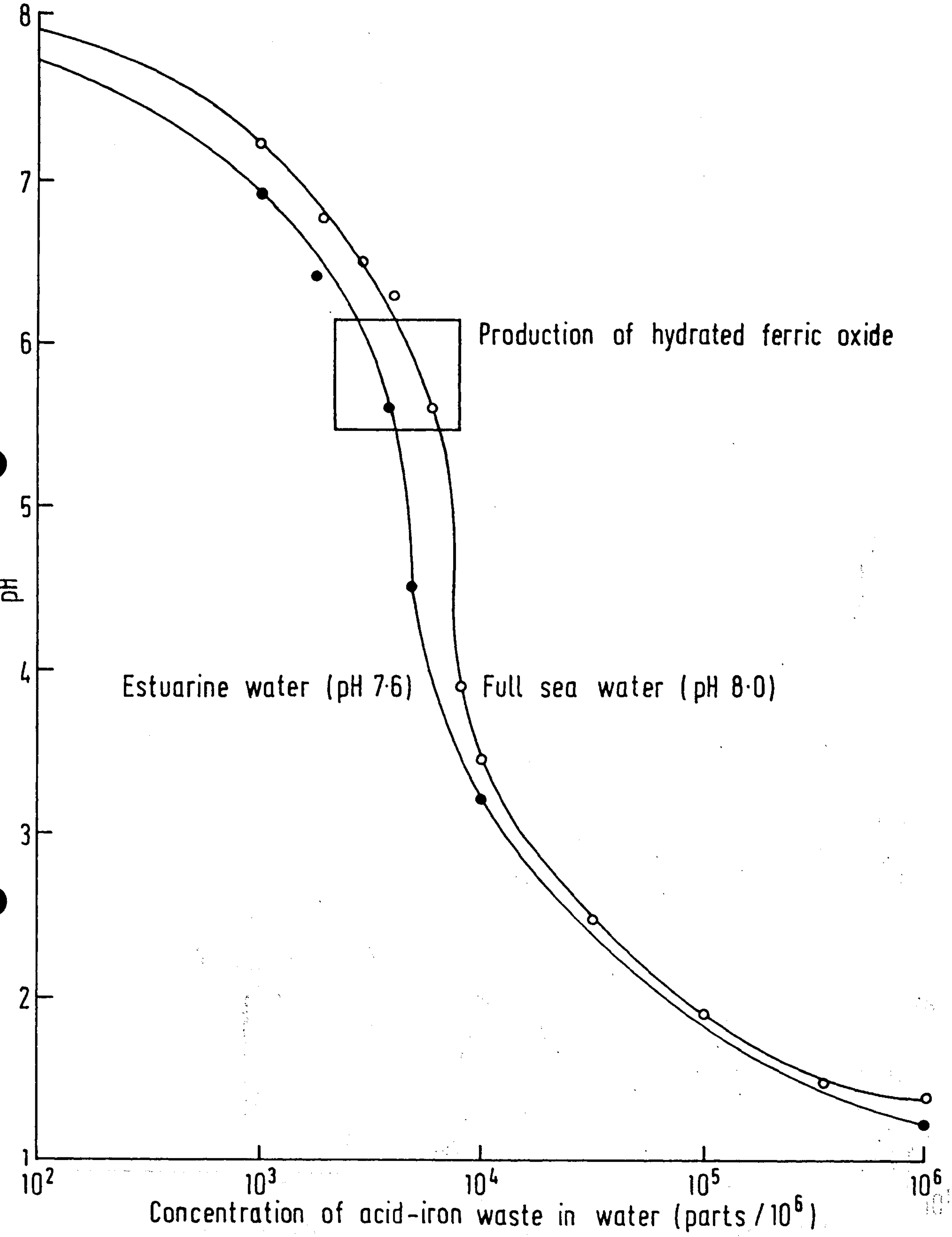

Figure 1. Changes in the pH of sea water due to acid-iron waste.

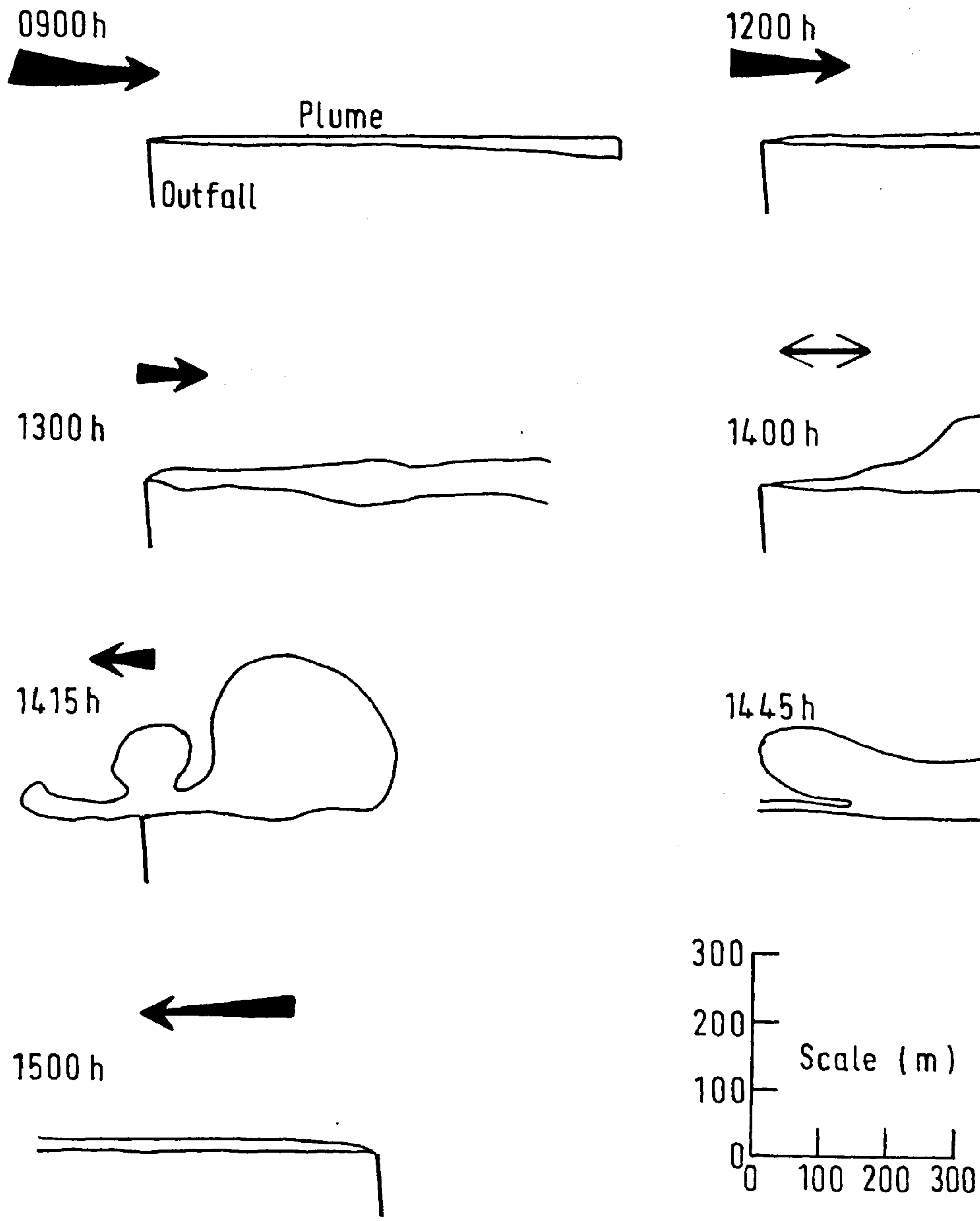

Figure 2. Changes in the shape of the effluent plume, as observed during part of a tidal cycle. High water 07.50 h, low water 14.00 h. The magnitude and direction of the main water flow is indicated by the arrows.

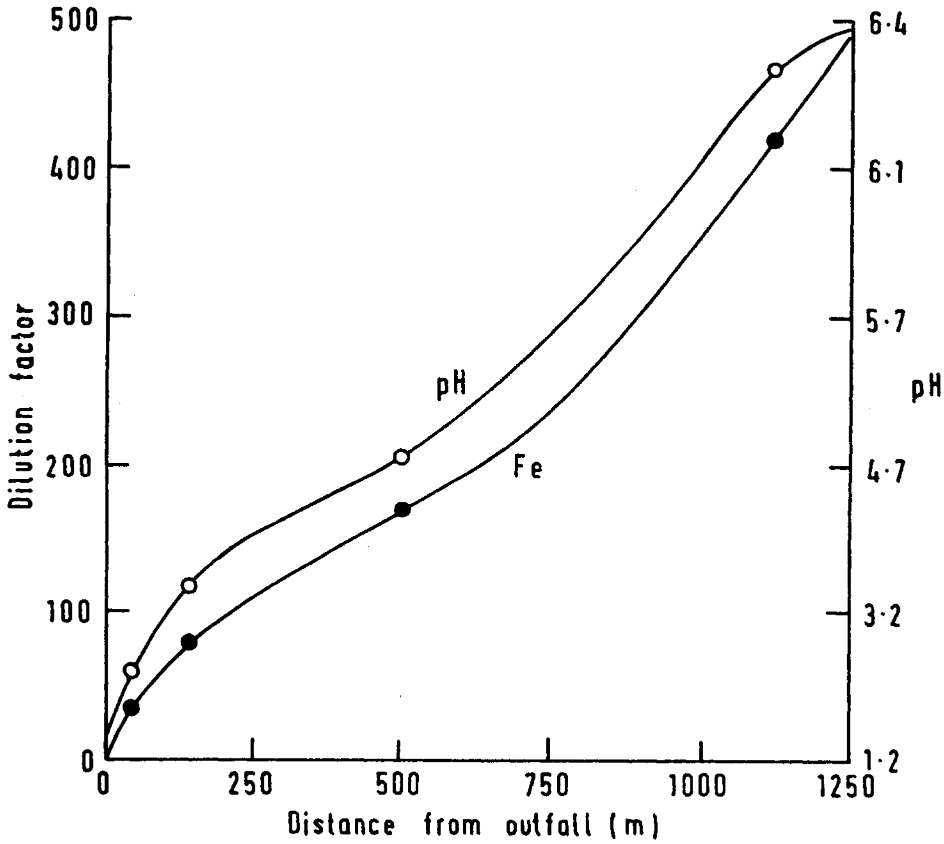

Figure 3. The dilution of the waste along the plume two hours before low water. Based on pH values and iron content.

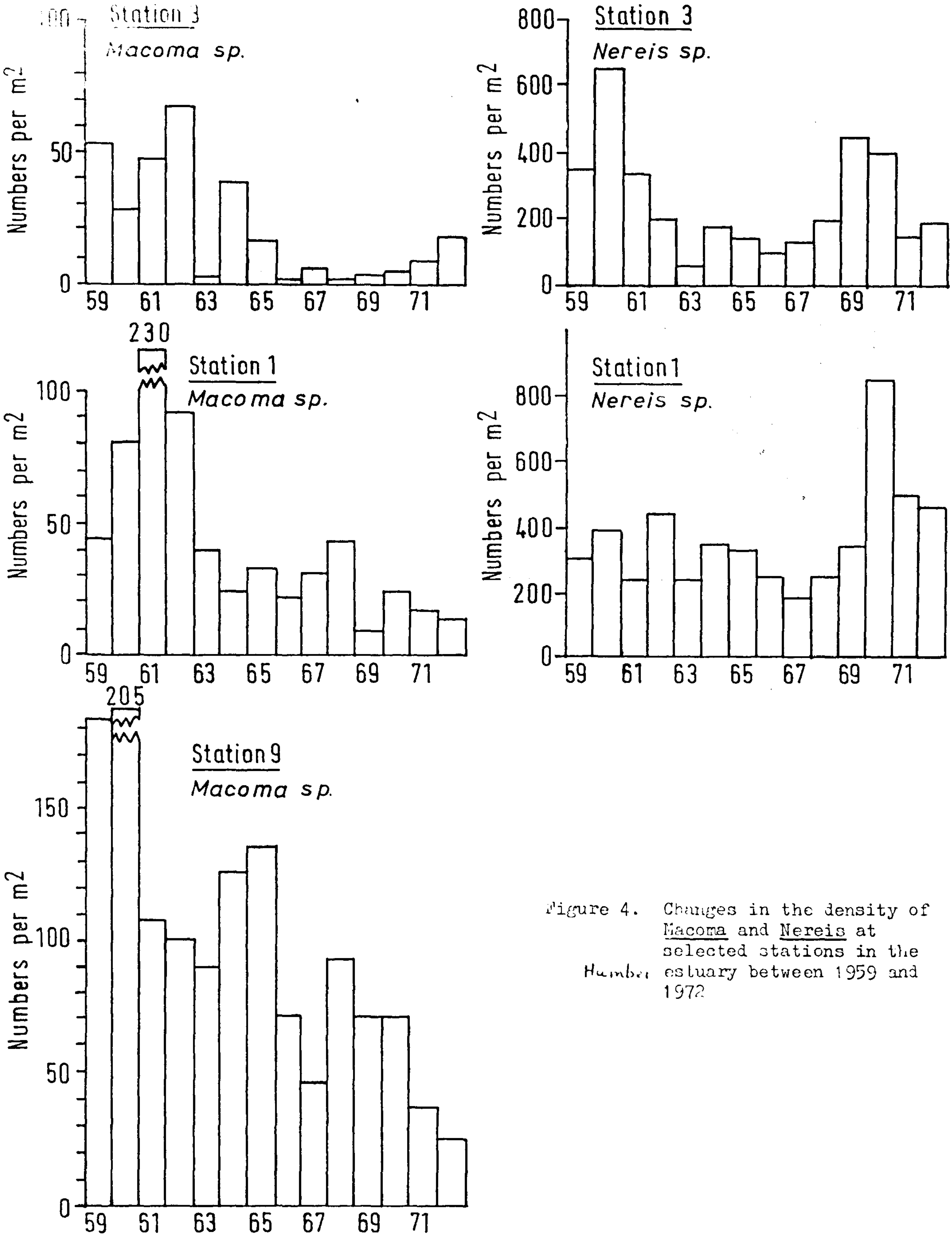

Figure 4. Changes in the density of *Macoma* and *Nereis* at selected stations in the Humber estuary between 1959 and 1972

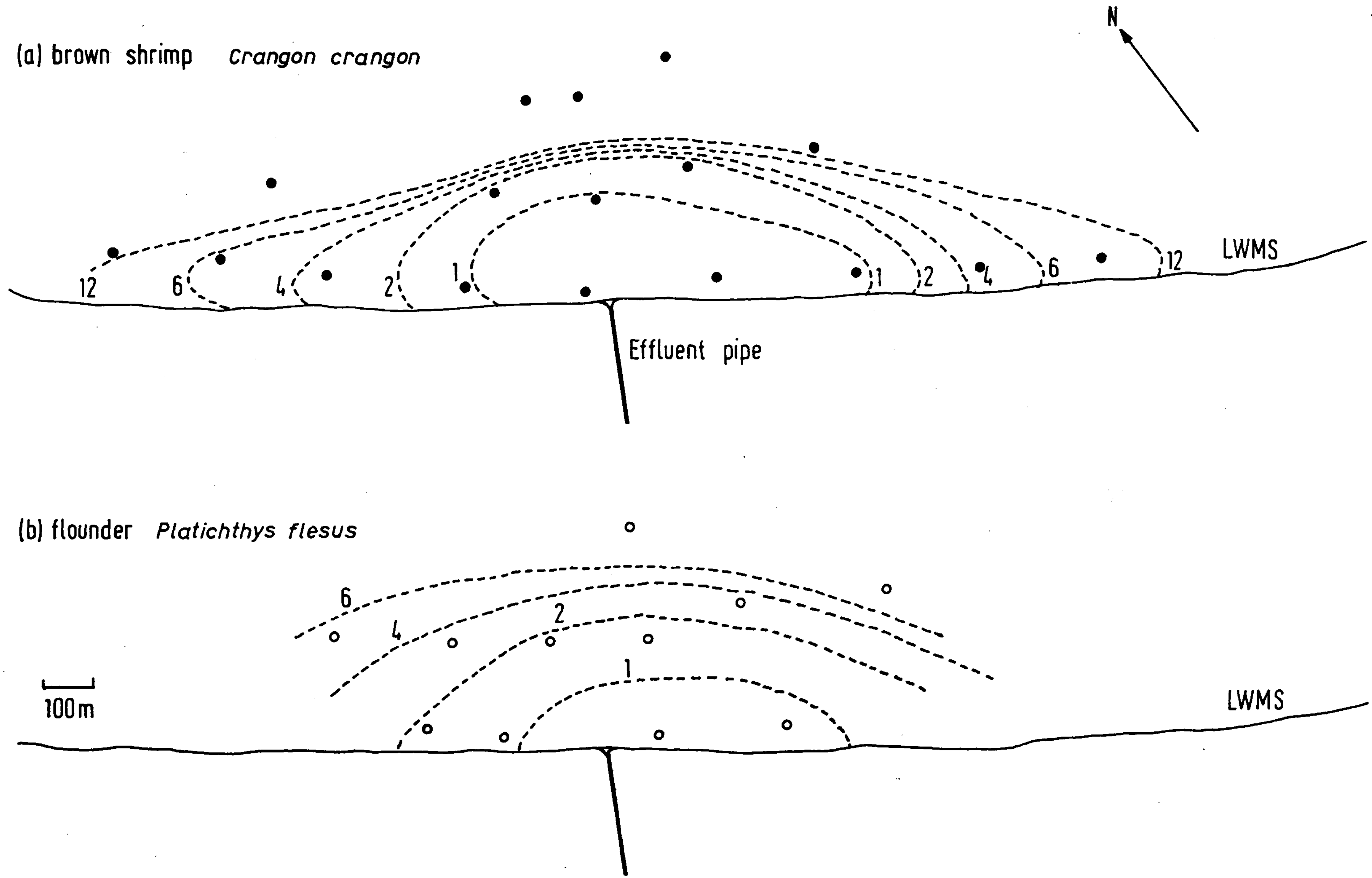

Figure 5. Areas of acute toxicity to shrimps and fish held in cages. Numbered isopleths show the period of exposure (in tidal cycles) required to kill 50% of the animals.

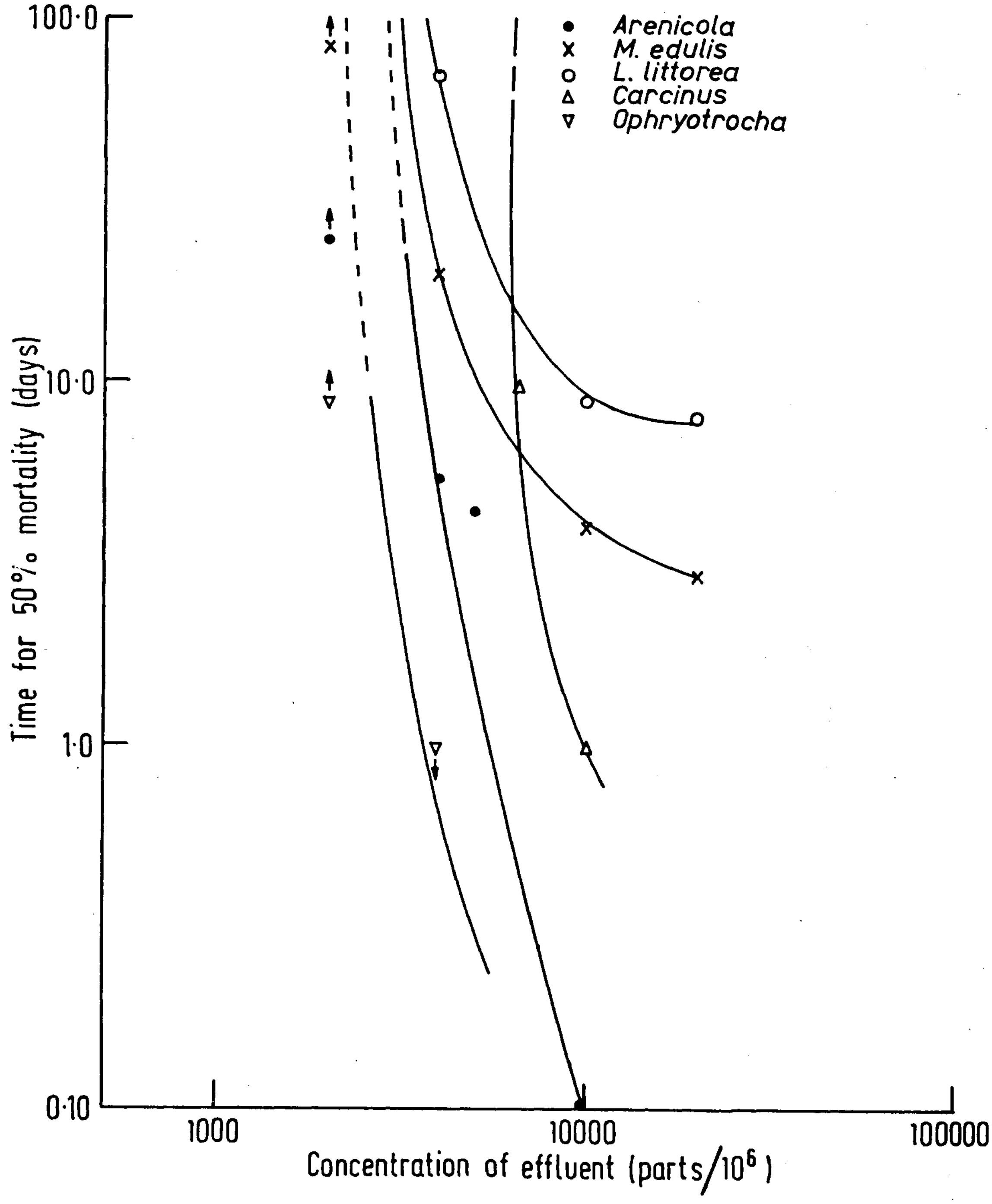

Figure 6. The acute toxicity of acid-iron waste to some marine and estuarine organisms at 15°C

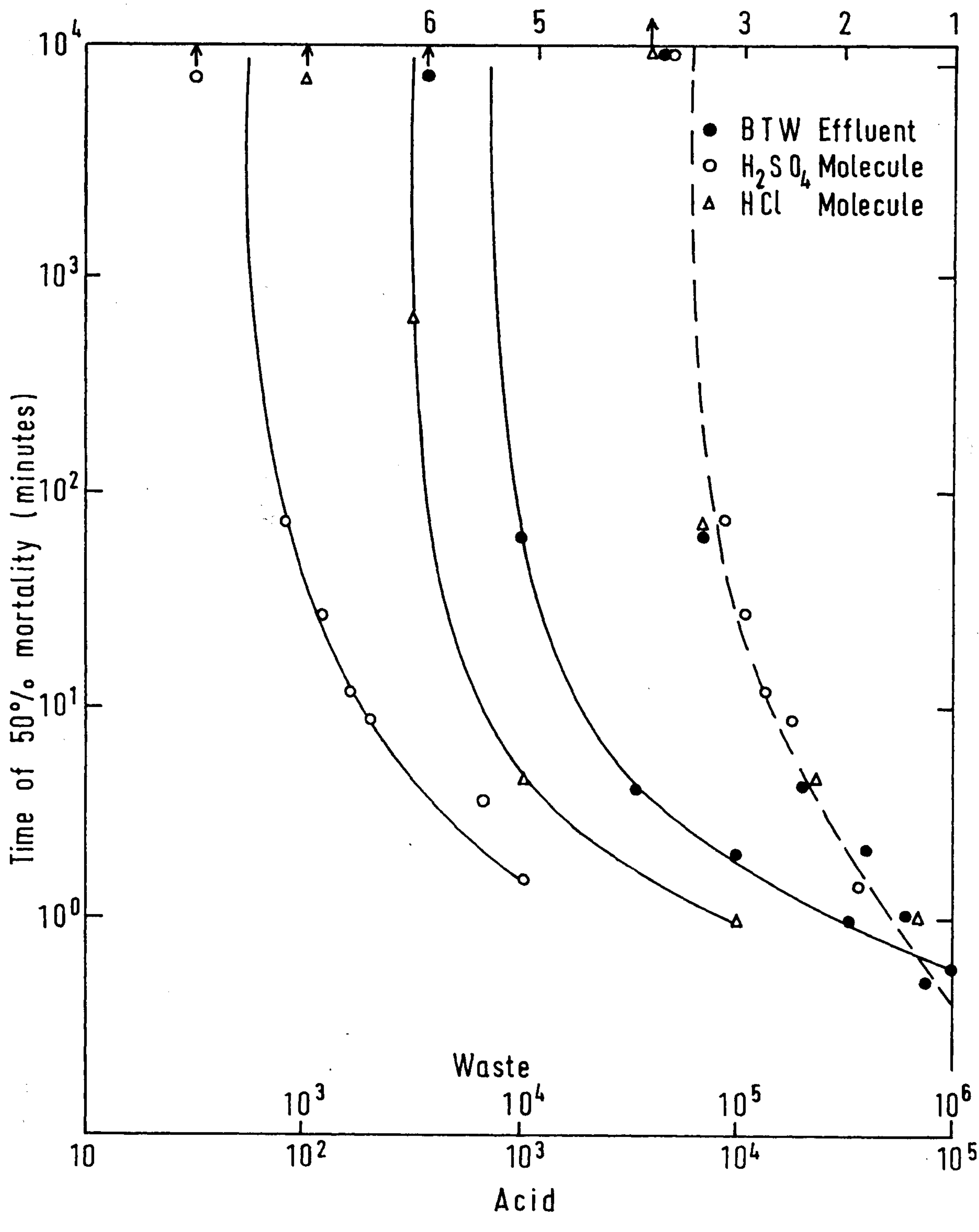

Figure 7. The toxicity of acid-iron waste to brown shrimp at 15°C compared with the toxicities of sulphuric acid and hydrochloric acid on the basis of concentration (solid lines) and pH (broken line).

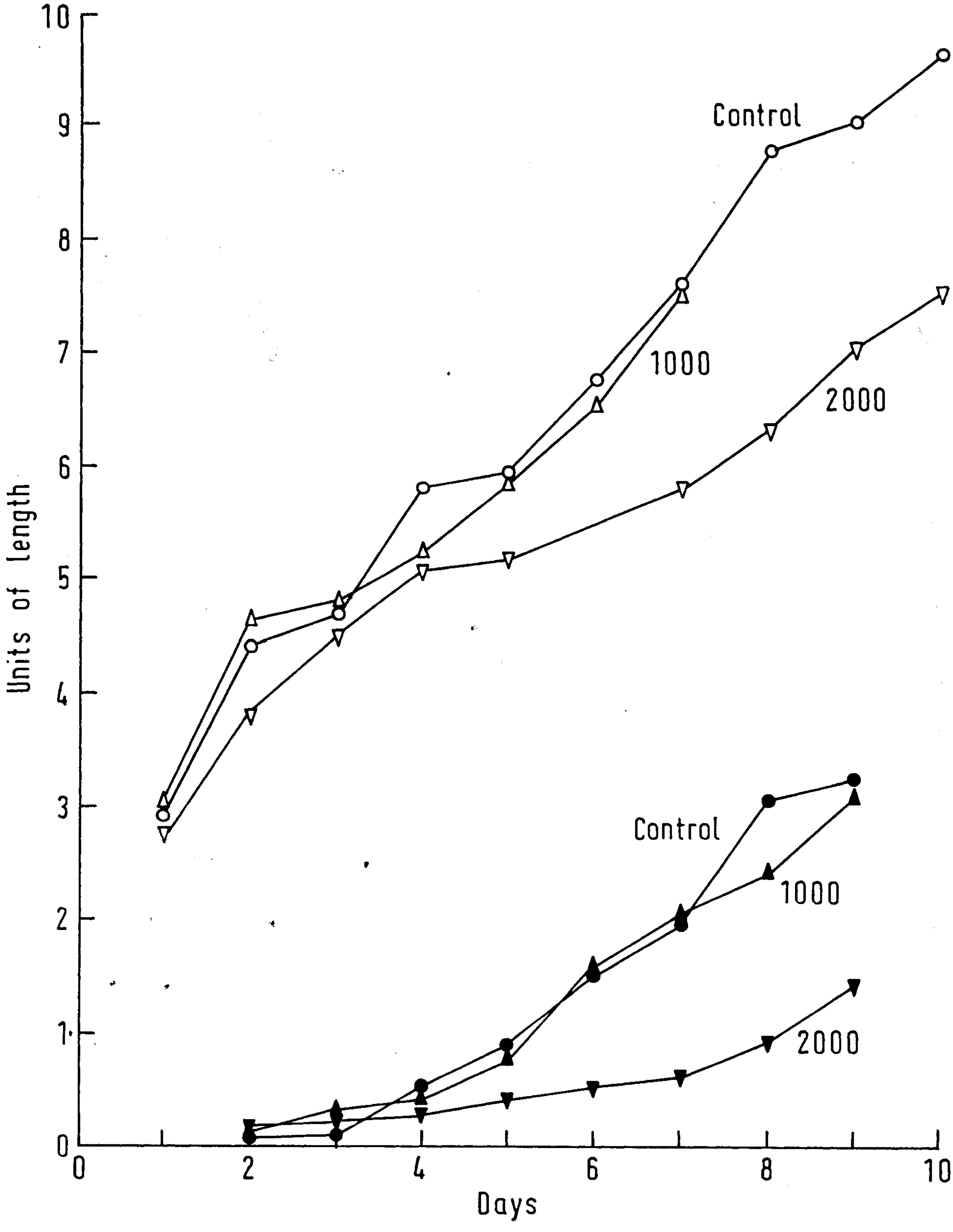

Figure 8. The effects of different concentrations of acid-iron waste (parts/10^6) on the growth of Artemia (open points) and Ophryotrocha (solid points).

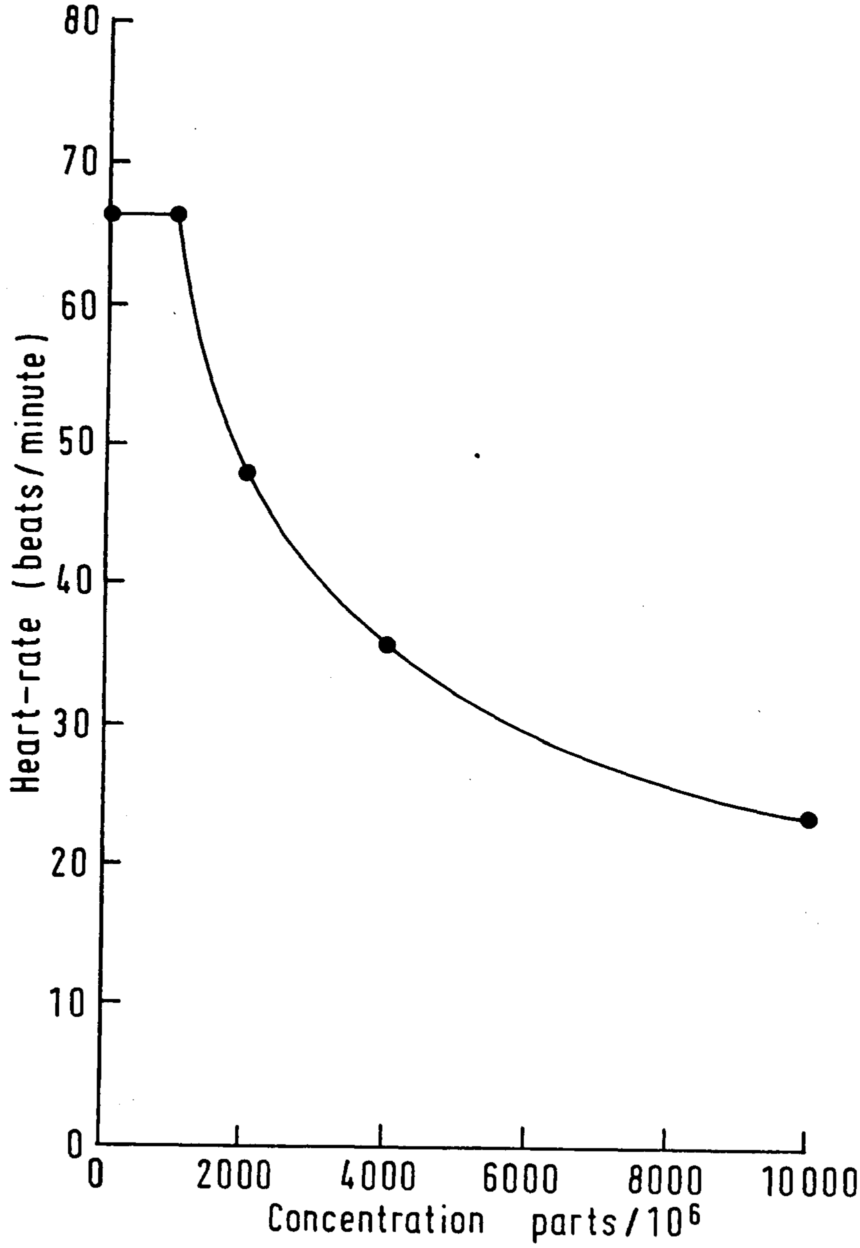

Figure 9. Heart-rate of *Agonus cataphractus* after 1 hours' immersion in various concentrations of acid-iron waste

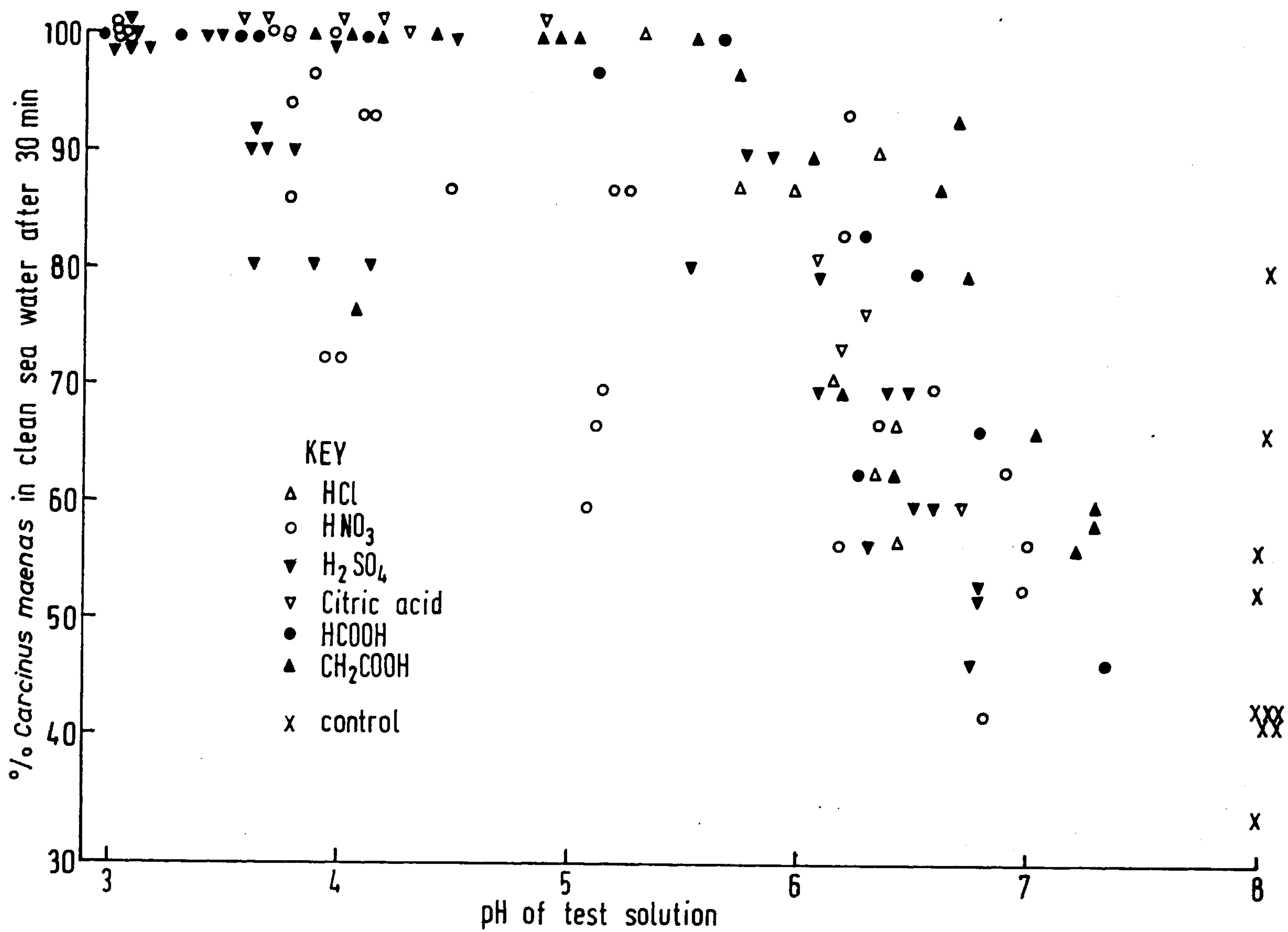

Figure 10. The distribution of *Carcinus* after 30 min between clean sea water and acidified sea water in a choice chamber